

Ag^I, Cd^{II}, and Hg^{II} complexes with 2,5-bis(pyridyl)pyrazine ligands: syntheses, spectral analyses, single crystal, and powder X-ray analyses

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2,5-Bis(4-pyridyl)pyrazine (*4-bppz*) and 2,5-bis(3-pyridyl)pyrazine (*3-bppz*) have been synthesized and characterized spectroscopically and crystallographically. *4-bppz* [unit cell: $a = 7.319(1)$, $b = 5.746(1)$, $c = 12.756(2)$ Å, $\beta = 93.16(1)^\circ$; space group: $P2_1/a$] was characterized by X-ray single crystal diffraction methods while the structure of *3-bppz* [unit cell: $a = 10.9148(4)$, $b = 4.5722(1)$, $c = 11.4462(2)$ Å, $\beta = 109.571(2)^\circ$; space group: $P2_1/c$] was determined from laboratory X-ray powder diffraction data. In these compounds, the pyrazine ring contains two symmetrically attached pyridine substituents with the nitrogen atom in the *para* positions for *4-bppz* and in the *meta* positions for *3-bppz*. Both compounds possess C_i symmetry with the pyridine rings twisted by 17.7° (*4-bppz*) and 2.6° (*3-bppz*) with respect to the pyrazine ring. *4-bppz* was used in the formation of coordination compounds with silver(I) and cadmium(II). The silver(I) complex $[\text{Ag}(\text{OAc})(4\text{-}bppz)]_n$ (**1**) [unit cell: $a = 8.472(1)$, $b = 13.051(1)$, $c = 19.063(2)$ Å, $\beta = 109.96(1)^\circ$; space group: $P2_1/c$] is characterized by the formation of a perfectly linear chain containing the silver ions bridged by the ligand molecule, the latter using its pyridine nitrogen donor atoms for coordination. A pair of chains is interconnected by silver–silver interactions, the silver coordination sphere being completed by acetate anions. A similar one-dimensional coordination polymer, $[\text{Cd}(\text{OAc})_2(4\text{-}bppz)(\text{MeOH})]_n$ (**2**) [unit cell: $a = 8.680(1)$, $b = 10.035(1)$, $c = 13.445(1)$ Å, $\alpha = 77.35(1)$, $\beta = 71.17(1)$, $\gamma = 80.14(1)^\circ$; space group: $P\bar{1}$], was obtained by the reaction of *4-bppz* with $\text{Cd}(\text{OAc})_2$. Ligand *3-bppz* forms an analogous cadmium(II) complex, $[\text{Cd}(\text{OAc})_2(3\text{-}bppz)(\text{MeOH})]_n$ (**3**) [unit cell: $a = 9.306(1)$, $b = 9.733(1)$, $c = 11.550(1)$ Å, $\alpha = 87.86(1)$, $\beta = 76.73(1)$, $\gamma = 85.91(1)^\circ$; space group: $P\bar{1}$], containing the molecules arranged in double *zigzag* chains. The reaction of *3-bppz* with HgI_2 leads surprisingly to a binuclear complex, $[\text{Hg}_2\text{I}_4(3\text{-}bppz)_2]$ (**4**) [unit cell: $a = 17.555(1)$, $b = 12.973(1)$, $c = 16.195(1)$ Å, $\beta = 115.32(1)^\circ$; space group: $C2/c$]. Two ligand molecules are bridged by two mercury(II) ions forming a cyclic structure, the tetrahedral coordination sphere of the metal being completed by iodide anions.

KEY WORDS: Pyrazine; coordination polymers; powder diffraction.

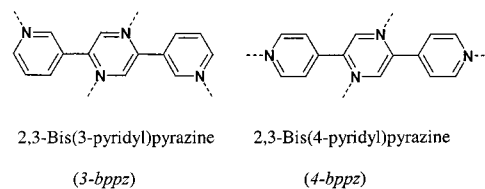
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Introduction

During the last years an effort has been made to construct inorganic supramolecular arrays based on covalent interactions¹ or hydrogen bonding² with the aim of designing functional materials. Much work has been devoted to the development of synthetic strategies to form novel 2D and 3D networks, which may have potential applications in many areas, for example $\{[\text{Zn}(4,4'\text{-bpy})_2](\text{SiF}_6)\}_n$ ³ and $\{[\text{Cu}(4,4'\text{-bpy})_2](\text{SiF}_6)\}_n$ ⁴ which contain square channels for the intercalation of guest molecules and diamondoid networks that offer considerable potential in the design of solids possessing finetunable bulk polarity.⁵ The choice of the bridging ligand and the coordination preference of the metal are fundamental requirements for the formation of such coordination polymers. For example, reactions using copper(I) and silver(I) salts with various linear bridging ligands resulted in adamantoid (super-diamondoid) structures in which the degree of interpenetration was found to be dependant on the length of the bridging ligand.⁶ Pyrazine⁷ and bipyridine ligands such as 4,4'-bipyridine⁸ and 3,3'-bipyridine⁹ have been widely used in the construction of microporous materials but larger spacer molecules such as 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine¹⁰ or 3,6-bis(3-pyridyl)-1,2,4,5-tetrazine¹¹ have also been used. In the reactions with silver(I), zinc(II), and cadmium(II), different types of complexes were obtained such as one- or two-dimensional polymers. The choice of the anion seems to be important for the product formation. One of the aims of this work is to create cavities, channels or interlayer spaces for the intercalation of guest molecules. The fixation of guest molecules within the host structure is often realized by the formation of hydrogen bonds between the two parts of the structure. This means that the knowledge of the capability of such ligands participating in such directed interactions is fundamental for crystal engineering.

We are particularly interested in the construction of multidimensional networks using pyrazine derivatives which results in versatile



Scheme 1. Possible coordination forms for 3-bppz and 4-bppz.

product formation.¹² The use of 2,5-bis(2-pyridyl)pyrazine as a bridging ligand between zinc(II) ions produced an interesting triangular system incorporating water molecules within the triangle.¹³ In this study we choose the ligands 2,5-bis(3-pyridyl)pyrazine (3-bppz) and 2,5-bis(4-pyridyl)pyrazine (4-bppz) for their potential ability to form coordination polymers involving both the pyridine and pyrazine nitrogen atoms in coordination (Scheme 1).

2,5-Bis(4-pyridyl)pyrazine was first synthesized in 1953 by Van der Meer *et al.*¹⁴ followed by Cymerman-Craig and Willis¹⁵ in 1955. No complex chemistry is known for this compound or to our knowledge for the new ligand 2,5-bis(3-pyridyl)pyrazine. Here we present the first results obtained for the reactions of these ligands with some d⁹, d¹⁰ transition metals such as silver(I), cadmium(II), and mercury(II).

Experimental section

Materials and methods.

The starting materials for the synthesis of 4-bppz and 3-bppz, namely 4- α -aminoacetylpyridine·2HCl and 3- α -aminoacetylpyridine·2HCl, were synthesized following preparative procedures of similar compounds described in the literature.¹⁶ The raw products, without further purification, were used for the synthesis of 4-bppz and 3-bppz. The relatively low yields (27% for 4-bppz and 13% for 3-bppz) could eventually be improved by purifying the starting materials. Nevertheless,

Table 1. Crystallographic Data for Compounds *4-bppz*, *3-bppz*, and **1**, **2**, **3**, and **4**

	<i>4-bppz</i>	<i>3-bppz</i> ^a	1	2	3	4
Empirical formula	C ₁₄ H ₁₀ N ₄	C ₁₄ H ₁₀ N ₄	C ₁₆ H ₁₃ N ₄ O ₂ Ag	C ₁₈ H ₁₆ N ₄ O ₄ Cd ·1.5CH ₃ OH	C ₁₈ H ₁₆ N ₄ O ₄ Cd ·CH ₃ OH	C ₂₈ H ₂₀ N ₈ I ₄ Hg ₂
CCDC deposit no.	CCDC-1003/6168	CCDC-1003/6169	CCDC-1003/6170	CCDC-1003/6171	CCDC-1003/6172	CCDC-1003/6173
<i>f w</i> , g mol ^{−1}	234.26	234.26	448.23	512.81	496.79	1377.30
<i>a</i> , Å	7.319(1)	10.9148(4)	8.472(1)	8.680(1)	9.306(1)	17.555(2)
<i>b</i> , Å	5.746(1)	4.5722(1)	13.051(1)	10.035(1)	9.733(1)	12.973(1)
<i>c</i> , Å	12.756(2)	11.4462(2)	19.063(2)	13.445(1)	11.550(1)	16.195(2)
α , deg	90	90	90	77.35(1)	87.86(1)	90
β , deg	93.16(1)	109.571(2)	109.96(1)	71.171(1)	76.73(1)	115.32(1)
γ , deg	90	90	90	80.135(1)	85.91(1)	90
<i>V</i> , Å ³	535.7(1)	538.21(1)	1981.1(3)	1075.0(2)	998.0(1)	3333.9(5)
<i>Z</i>	2	2	4	2	2	4
Space group	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)
<i>T</i> , K	153(2)	293(2)	153(2)	153(2)	153(2)	153(2)
ρ_{calc} , g cm ^{−3}	1.452	1.446	1.503	1.584	1.653	2.744
λ (Cu K α), Å	0.71073	1.5406	0.71073	0.71073	0.71073	0.71073
<i>R</i> 1 ^b / <i>R</i> p ^c	0.032 ^b	0.051 ^c	0.132 ^b	0.030 ^b	0.021 ^b	0.0246 ^b
<i>wR</i> 2 ^d / <i>R</i> _F ^e	0.077 ^d	0.061 ^e	0.300 ^d	0.080 ^d	0.050 ^d	0.055 ^d

^a Powder structure.^b $R1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$.^c $R_p = \sum |I_o - I_c| / \sum I_c$.^d $wR2 = \left[\sum w \left(\|F_o^2\| - \|F_c^2\| \right)^2 / \sum w F_o^4 \right]^{1/2}$.^e $R_F = (\|F_o\| - \|F_c\|) / (\|F_o\|)$.

the yield found for *4-bppz* is much higher (27%) than the yield reported (3%).¹⁴ All metal complexes were crystallized from very dilute reaction solutions containing small quantities of the starting materials. For this reason, no yields are reported. All other chemicals were used as received. Melting points were determined with a GALLENKAMP MFB-595 apparatus using samples in sealed tubes. The NMR spectra were recorded with a VARIAN GEMINI 2000 (200 MHz); the chemical shifts (δ) were reported in ppm values relative to tetramethylsilane as the internal standard. Coupling constants (*J*) are given in Hertz (Hz). The following abbreviations were used: s (singlet) and d (doublet). Elemental analyses were performed by the ISF Abteilung Chemie CH-1705 Fribourg. Electron impact mass spectroscopy was recorded on a NERMAG RC30-10 system. The electronic beam energy used to carry out the EI was 70 eV. The infrared spectra were obtained using a PERKIN-ELMER FT-IR 1720 X spectrophotometer with

a potassium bromide disc containing a trace of the sample. The absorption frequency range studied was between 4000 and 400 cm^{−1}. Peaks were labelled with the following abbreviations: b (broad), m (medium), s (strong), and w (weak).

General preparation method for

2,5-bis(pyridyl)pyrazine (4-bppz and 3-bppz)

An aqueous NH₃ solution (24%, 19 mL, 0.27 mol) was added to a solution of α -aminoacetylpyridine·2HCl (11.8 g, 57 mmol; 4- α -aminoacetylpyridine·2HCl for *4-bppz*, 3- α -aminoacetylpyridine·2HCl for *3-bppz*) in water (120 mL) at room temperature. The solution turned red and the orange precipitate which formed rapidly was filtered off after stirring for 3 h, washed with cold water, and dried over silica gel.

4-bppz. Yield 1.77 g (27%). After recrystallization in a water/ethanol mixture, light yellow

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotopic Displacement Parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
<i>4-bppz</i>				
N(1)	10468(1)	−2040(2)	−515(1)	22(1)
N(2)	7963(1)	3(2)	4209(1)	23(1)
C(1)	9972(2)	−2047(2)	474(1)	22(1)
C(2)	9501(1)	−32(2)	1003(1)	17(1)
C(3)	8963(1)	−54(2)	2109(1)	17(1)
C(4)	9378(2)	−1911(2)	2785(1)	20(1)
C(5)	8853(2)	−1804(2)	3812(1)	23(1)
C(6)	7581(2)	1789(2)	3557(1)	22(1)
C(7)	8043(2)	1837(2)	2519(1)	20(1)
<i>3-bppz</i>				
N(1)	0.9423(6)	0.1208(14)	0.8843(5)	25
N(2)	0.6502(6)	0.6742(15)	1.0356(6)	25
C(1)	0.9004(6)	0.1957(18)	0.9820(9)	25
C(2)	1.0374(9)	−.0664(19)	0.9034(7)	25
C(3)	0.7969(6)	0.4174(14)	0.9529(7)	25
C(4)	0.7315(8)	0.5321(20)	0.8363(6)	25
C(5)	0.6312(8)	0.7295(17)	0.8256(6)	25
C(6)	0.6012(6)	0.8037(19)	0.9282(7)	25
C(7)	0.7543(7)	0.5113(15)	1.0553(6)	25
[Ag(OAc)(4- <i>bppz</i>) _n (1)]				
Ag(1)	1485(2)	9260(1)	128(1)	38(1)
O(1)	2998(15)	9059(8)	1557(6)	43(3)
O(2)	946(13)	10201(9)	1393(6)	42(3)
N(1)	−3809(15)	4749(10)	−634(7)	35(1)
N(2)	−2790(15)	3449(10)	577(7)	35(1)
N(3)	142(15)	7824(10)	62(7)	35(1)
N(4)	3095(15)	10576(10)	−19(7)	35(1)
C(1)	−2483(15)	4991(10)	−17(7)	25(1)
C(2)	−1972(15)	4384(11)	590(7)	25(1)
C(3)	−4096(15)	3206(11)	−33(7)	25(1)
C(4)	−4614(15)	3875(10)	−644(7)	25(1)
C(5)	−1600(16)	5994(10)	14(7)	28(1)
C(6)	−1996(16)	6645(10)	−607(8)	28(1)
C(7)	−1115(16)	7541(11)	−546(8)	28(1)
C(8)	557(16)	7189(11)	641(7)	28(1)
C(9)	−292(16)	6250(11)	633(7)	28(1)
C(10)	2696(17)	11059(11)	−632(8)	32(1)
C(11)	3670(17)	11949(11)	−684(8)	32(1)
C(12)	4972(18)	12246(12)	−59(8)	32(1)
C(13)	5306(18)	11662(11)	585(8)	32(1)
C(14)	4273(17)	10905(11)	621(8)	32(1)
C(15)	2050(20)	9680(13)	1801(8)	38(4)
C(16)	2480(30)	9676(18)	2628(10)	73(7)
[Cd(OAc)(4- <i>bppz</i>)(MeOH)] _n (2)				
Cd(1)	4406(1)	9303(1)	3977(1)	23(1)
O(1)	3836(3)	8264(2)	2679(2)	38(1)
O(1M)	4560(4)	13003(3)	−915(3)	76(1)
O(2)	2142(3)	9986(3)	3315(2)	40(1)
O(2M)	3496(8)	15379(5)	3390(5)	60(2)
O(3)	3604(3)	11010(2)	5028(2)	41(1)
O(4)	3134(3)	12288(2)	6236(2)	32(1)

Table 2. Continued

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N(1)	9018(5)	15677(3)	−1216(3)	60(1)
N(2)	9980(3)	12887(3)	−790(2)	31(1)
N(3)	2954(3)	7805(2)	5398(2)	29(1)
N(4)	5905(3)	10806(2)	2568(2)	27(1)
C(1)	10351(4)	15105(3)	−1878(3)	34(1)
C(1M)	3960(5)	11924(4)	−93(4)	61(1)
C(2)	10829(4)	13700(3)	−1634(2)	31(1)
C(2M)	2529(8)	15242(6)	2847(6)	42(2)
C(3)	8623(4)	13463(3)	−145(2)	31(1)
C(4)	8164(5)	14871(4)	−372(3)	58(1)
C(5)	11247(4)	16015(3)	−2824(2)	31(1)
C(6)	10630(4)	17385(3)	−3068(3)	31(1)
C(7)	1498(4)	8228(3)	6054(2)	30(1)
C(8)	3531(5)	6484(3)	5635(3)	45(1)
C(9)	12734(5)	15575(3)	−3514(3)	50(1)
C(10)	7667(4)	12574(3)	785(2)	26(1)
C(11)	6308(4)	13066(3)	1566(3)	41(1)
C(12)	5487(4)	12178(3)	2416(3)	41(1)
C(13)	7207(4)	10327(3)	1827(2)	27(1)
C(14)	8098(3)	11155(3)	951(2)	29(1)
C(15)	2578(4)	9137(4)	2702(3)	36(1)
C(16)	1597(5)	9133(5)	1960(3)	58(1)
C(17)	2731(4)	11939(3)	5525(2)	29(1)
C(18)	1205(5)	12627(5)	5262(4)	65(1)
[Cd(OAc)(3- <i>bppz</i>)(MeOH)] _n (3)				
Cd(1)	1609(1)	3819(1)	9278(1)	17(1)
N(1)	1915(2)	10327(2)	3829(2)	21(1)
N(2)	1476(2)	7527(2)	4932(2)	23(1)
N(3)	460(2)	1971(2)	10657(2)	18(1)
N(4)	2768(2)	5799(2)	8105(2)	19(1)
O(1)	3921(2)	3054(2)	9901(1)	27(1)
O(2)	3493(2)	2331(2)	8325(1)	26(1)
O(3)	−869(2)	4886(2)	9164(2)	33(1)
O(4)	230(2)	3742(2)	7744(1)	26(1)
C(1)	2501(3)	9733(2)	4769(2)	20(1)
C(2)	2288(2)	8340(2)	5331(2)	18(1)
C(3)	882(3)	8130(2)	3999(2)	23(1)
C(5)	409(3)	173(2)	12409(2)	18(1)
C(4)	1089(2)	9525(2)	3438(2)	17(1)
C(6)	−863(3)	−335(2)	12222(2)	20(1)
C(7)	−1471(3)	351(2)	11265(2)	20(1)
C(8)	−784(3)	1492(2)	10508(2)	20(1)
C(9)	1036(2)	1321(2)	11592(2)	18(1)
C(10)	2903(2)	7686(2)	6393(2)	18(1)
C(11)	4046(3)	8247(2)	6731(2)	21(1)
C(12)	4537(3)	7560(2)	7747(2)	23(1)
C(13)	3873(3)	6351(2)	8413(2)	21(1)
C(14)	2312(3)	6460(2)	7109(2)	19(1)
C(21)	4326(3)	2401(2)	9040(2)	23(1)
C(22)	5825(3)	1665(3)	8841(3)	47(1)
C(23)	−804(3)	4539(2)	8160(2)	21(1)
C(24)	−1942(4)	5136(3)	7437(3)	45(1)
C(1ME)	3492(4)	3289(3)	5415(3)	54(1)
O(1ME)	4005(2)	1977(2)	5961(2)	36(1)

Table 2. Continued

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
[HgI ₂ (3- <i>bppz</i>) ₂] (4)				
Hg(1)	2422(1)	5098(1)	1701(1)	28(1)
I(1)	3841(1)	4215(1)	2849(1)	36(1)
I(2)	884(1)	5792(1)	1287(1)	36(1)
N(1)	3655(3)	2407(4)	−1244(3)	27(1)
N(2)	5094(3)	3642(4)	−472(3)	27(1)
N(3)	2287(3)	4269(3)	290(3)	21(1)
N(4)	3025(3)	6682(4)	1358(3)	30(1)
C(1)	3686(3)	3230(4)	−729(3)	20(1)
C(2)	4398(3)	3836(5)	−355(3)	26(1)
C(3)	4932(3)	7189(4)	975(3)	22(1)
C(4)	5655(3)	7794(5)	1359(4)	28(1)
C(5)	2919(3)	3477(4)	−609(3)	20(1)
C(6)	2119(3)	3204(4)	−1266(3)	26(1)
C(7)	1418(3)	3477(5)	−1136(3)	28(1)
C(8)	1528(3)	4019(4)	−350(3)	24(1)
C(9)	2959(3)	4001(4)	168(3)	23(1)
C(10)	4170(3)	7399(5)	1124(3)	25(1)
C(11)	3856(4)	8388(5)	1123(4)	33(1)
C(12)	3124(4)	8496(5)	1223(4)	36(1)
C(13)	2716(3)	7622(5)	1330(4)	31(1)
C(14)	3735(3)	6582(5)	1259(3)	27(1)

crystals were obtained. Melting point 250°C (241°C¹⁴, 231°C¹⁵). Anal. calc for C₁₄H₁₀N₄ (*M*_r = 234.3 g/mol): C, 71.71; H, 4.27; N, 23.90. Found: C, 70.24; H, 4.26; N, 23.47%. IR (KBr) ν (C=N, C=C): 1599 (s), 1555 (m), 1507 (w), 1474 (s), 1414 (s) cm^{−1}. RMN ¹H (CD₃OD) δ : 9.44 (s, 2H), 8.76 (dd, ³*J* = 4.57, ⁵*J* = 1.64, 4H), 8.25 (dd, ³*J* = 4.58, ⁵*J* = 1.64, 4H) ppm. RMN ¹³C (CDCl₃) δ : 151.2 (4C), 150.1 (2C), 143.4 (2C), 142.2 (2C), 121.2 (4C). ESI MS *m/z*: 235.3 ([M+H]⁺).

3-*bppz*. Yield 1.1 g (13%), mp 233°C. Anal. calc for C₁₄H₁₀N₄ (*M*_r = 234.3 g/mol): C, 71.71; H, 4.27; N, 23.90. Found: C, 71.40; H, 4.33; N, 24.00%. IR (KBr) ν (C=N, C=C): 1587 (m), 1573 (m), 1504 (w), 1474 (m), 1418 (s) cm^{−1}. RMN ¹H (CDCl₃) δ : 9.34 (dd, ⁴*J* = 2.38, ⁵*J* = 0.92, 2H), 9.18 (s, 2H), 8.76 (dd, ³*J* = 4.76, ⁴*J* = 1.65, 2H), 8.43 (ddd, ³*J* = 8.06, ⁴*J* = 2.38, ⁵*J* = 1.65, 2H), 7.51 (ddd, ³*J* = 8.06, ³*J* = 4.76, ⁵*J* = 0.92, 2H) ppm. RMN ¹³C (CDCl₃) δ : 150.9 (2C), 149.1 (2C), 148.1 (2C), 141.4 (2C), 134.3 (2C), 131.7 (2C), 123.9 (2C). ESI MS *m/z*: 235.0 ([M + H]⁺).

Preparation of [Ag(OAc)(4-*bppz*)]_n (1)

4-*bppz* (50 mg, 0.21 mmol) in methanol (10 mL) was added to a silver acetate (143 mg, 0.84 mmol) solution in methanol/acetonitrile (40 mL/20 mL). The precipitate which formed immediately was filtered off. This insoluble, amorphous solid was not characterized further. The slow evaporation of the filtrate gave transparent light yellow crystals. IR (KBr) ν (C=N, C=C, OAc[−]): 1570 (s, b), 1474 (s), 1409 (s, b), 1342 (m) cm^{−1}.

Preparation of

{[Cd(OAc)₂(4-*bppz*)](MeOH)_{1.5}]_n (2)

4-*bppz* (10 mg, 0.04 mmol) was dissolved in dichloromethane (5 mL) and placed in a tube. Cadmium acetate (11.4 mg, 0.04 mmol) in methanol (5 mL) was layered gently over the solution containing the organic ligand. After 1 day, small yellow crystals were formed at the interface of the two phases. IR (KBr) ν (C=N, C=C, OAc[−]): 1610 (s), 1570 (s, b), 1475 (s), 1430 (s), 1424 (s, b), 1354 (s) cm^{−1}.

Preparation of

{[Cd(OAc)₂(3-*bppz*)](MeOH)_n (3)

Compound **3** was prepared following the same procedure as for compound **2** using 10 mg of 3-*bppz* (0.04 mmol). IR (KBr) ν (C=N, C=C, OAc[−]): 1565 (s, b), 1504 (m), 1464 (s), 1424 (s, b), 1343 (s) cm^{−1}.

Preparation of [HgI₂(3-*bppz*)₂](4)

3-*bppz* (25 mg, 0.1 mmol) dissolved in a methanol/dichloromethane solution (4 mL/1 mL) was added to a solution of HgI₂ (48.5 mg, 0.1 mmol) in methanol (15 mL). The resulting mixture was filtered and red-brown crystals were obtained after slow evaporation of the solvent. IR (KBr) ν (C=N, C=C): 1596 (s), 1576 (w), 1498 (w), 1466 (s), 1428 (m), 1417 (s) cm^{−1}.

Table 3. Important Bond Distances (Å) and Angles (°) for Complexes 1–4

[Ag(OAc)(4-<i>bppz</i>)]_n (1)			
Ag(1)—N(3)	2.173(13)	N(3)—Ag(1)—O(4)	166.0(5)
Ag(1)—N(4)	2.270(12)	N(3)—Ag(1)—O(1)	92.0(4)
Ag(1)—O(1)	2.598(11)	N(4)—Ag(1)—O(1)	95.9(4)
Ag(1)—Ag(1)a	3.077(3)	N(3)—Ag(1)—Ag(1)a	98.5(3)
		N(4)—Ag(1)—Ag(1)a	89.9(3)
		O(1)—Ag(1)—Ag(1)a	108.3(3)
[Cd(OAc)(4-<i>bppz</i>)(MeOH)]_n (2)			
Cd(1)—N(3)	2.309(3)	N(3)—Cd(1)—O(4)b	91.91(8)
Cd(1)—N(4)	2.321(3)	N(4)—Cd(1)—O(4)b	87.44(8)
Cd(1)—O(1)	2.431(2)	O(3)—Cd(1)—O(4)b	126.84(8)
Cd(1)—O(2)	2.351(2)	O(2)—Cd(1)—O(4)b	141.01(7)
Cd(1)—O(3)	2.331(2)	N(3)—Cd(1)—O(1)	92.51(8)
Cd(1)—O(4)b	2.414(2)	N(4)—Cd(1)—O(1)	88.42(8)
Cd(1)—O(3)b	2.448(2)	O(3)—Cd(1)—O(1)	146.77(8)
		O(2)—Cd(1)—O(1)	54.79(8)
N(3)—Cd(1)—N(4)	178.83(8)	O(4)b—Cd(1)—O(1)	86.27(7)
N(3)—Cd(1)—O(3)	89.38(8)	N(3)—Cd(1)—O(3)b	85.73(8)
N(4)—Cd(1)—O(3)	90.23(8)	N(4)—Cd(1)—O(3)b	93.10(8)
N(3)—Cd(1)—O(2)	91.74(9)	O(3)—Cd(1)—O(3)b	73.87(10)
N(4)—Cd(1)—O(2)	89.37(9)	O(2)—Cd(1)—O(3)b	165.65(8)
O(3)—Cd(1)—O(2)	92.00(9)	O(4)b—Cd(1)—O(3)b	53.29(7)
		O(1)—Cd(1)—O(3)b	139.36(7)
[Cd(OAc)(3-<i>bppz</i>)(MeOH)]_n (3)			
Cd(1)—N(3)	2.3154(17)	N(3)—Cd(1)—O(4)	95.58(6)
Cd(1)—N(4)	2.3225(18)	N(4)—Cd(1)—O(4)	90.32(6)
Cd(1)—O(3)c	2.3363(16)	O(3)c—Cd(1)—O(4)	124.85(6)
Cd(1)—O(2)	2.3816(17)	O(2)—Cd(1)—O(4)	89.18(5)
Cd(1)—O(4)	2.4300(15)	N(3)—Cd(1)—O(1)	89.51(6)
Cd(1)—O(1)	2.4341(16)	N(4)—Cd(1)—O(1)	88.26(6)
Cd(1)—O(3)	2.4665(19)	O(3)c—Cd(1)—O(1)	91.56(6)
		O(2)—Cd(1)—O(1)	54.36(5)
N(3)—Cd(1)—N(4)	172.73(6)	O(4)—Cd(1)—O(1)	143.47(6)
N(3)—Cd(1)—O(3)c	85.80(6)	N(3)—Cd(1)—O(3)	87.91(6)
N(4)—Cd(1)—O(3)c	87.35(6)	N(4)—Cd(1)—O(3)	92.33(6)
N(3)—Cd(1)—O(2)	93.26(6)	O(3)c—Cd(1)—O(3)	72.41(7)
N(4)—Cd(1)—O(2)	91.05(6)	O(2)—Cd(1)—O(3)	141.66(5)
O(3)c—Cd(1)—O(2)	145.92(6)	O(4)—Cd(1)—O(3)	52.63(5)
		O(1)—Cd(1)—O(3)	163.90(5)
[HgI₂(3-<i>bppz</i>)]₂ (4)			
Hg(1)—N(3)	2.443(4)	N(3)—Hg(1)—I(2)	103.40(10)
Hg(1)—N(4)	2.480(5)	N(4)—Hg(1)—I(2)	98.53(11)
Hg(1)—I(1)	2.6479(5)	N(3)—Hg(1)—I(1)	98.77(10)
Hg(1)—I(2)	2.6474(5)	N(4)—Hg(1)—I(1)	98.74(11)
N(3)—Hg(1)—N(4)	92.02(15)	I(2)—Hg(1)—I(1)	151.247(15)

Note: a: $-x, -y + 2, -z$; b: $-x + 1, -y + 2, -z + 1$; c: $-x, -y + 1, -z + 2$.

*X-ray data collection and structure solution for 4-*bppz*, 1, 2, 3, and 4*

Crystals of compounds 4-*bppz*, **1**, **2**, **3**, and **4** were mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995)

equipped with a one-circle φ goniometer and a graphite-monochromator. Data collection was performed at -120°C for all compounds using Mo K α radiation ($\lambda = 0.71073$ Å). Two hundred exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with

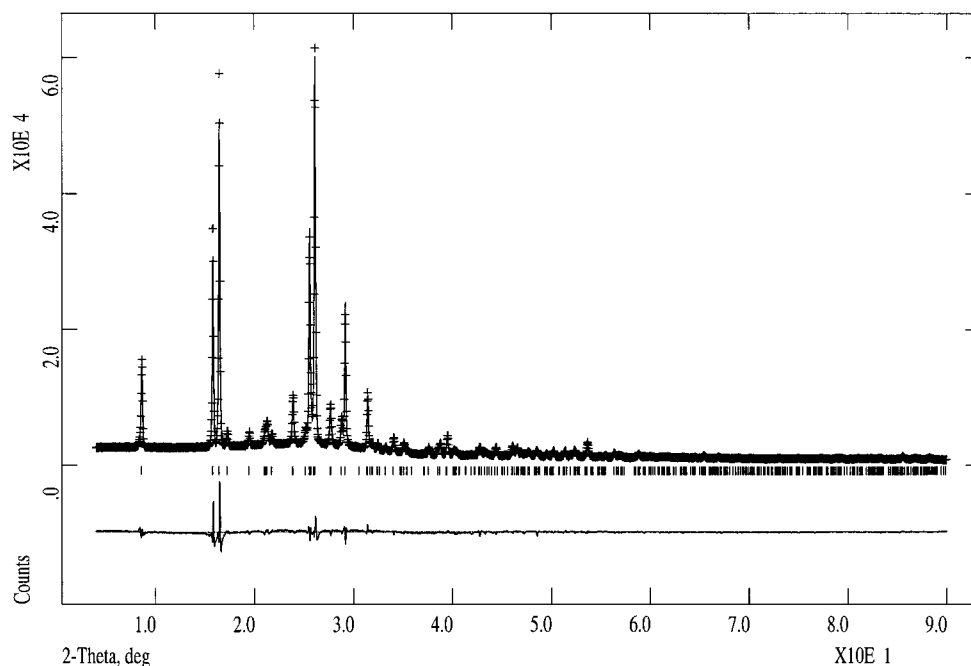


Fig. 1. Observed (+) and calculated (—) profiles for the Rietveld refinement for 2,5-bis(3-pyridyl)pyrazine (*3-bppz*). The bottom curve is the difference plot on the same intensity scale.

$0 < \varphi < 200^\circ$ and with the crystal oscillating through 1° in φ . The resolution was D_{\min} – D_{\max} 12.45–0.81 Å. The structures were solved by direct methods using the program SHELXS-97¹⁷ and refined by full matrix least squares on F^2 with SHELXL-97.¹⁸ The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. Compound **2** crystallizes with 1.5 molecules, compound **3** with one molecule of methanol per asymmetric unit. An empirical absorption correction was applied using DIFABS¹⁹ for compounds **1** ($T_{\min} = 0.327$, $T_{\max} = 0.756$) and **4** ($T_{\min} = 0.155$, $T_{\max} = 0.627$). Complex **1** was obtained as twinned crystals, therefore the structure resolution was poor which is reflected in the high R -values and relatively high standard uncertainties for bond distances and angles. Nevertheless it is interesting to compare its structure with those of similar compounds. Crystallographic details are given in Table 1, fractional coordinates of all compounds are listed in Table 2, and significant bond lengths and bond angles for compounds **1**, **2**, **3**, and **4** are

shown in Table 3. The figures were drawn using PLATON¹⁹ or ORTEP-3.²⁰

X-ray data collection and structure solution for 3-bppz

3-bppz was recrystallized in a methanol/water mixture and could only be obtained in microcrystalline form. Therefore, X-ray powder diffraction data were collected in transmission mode (0.5 mm rotating capillary) on a high resolution laboratory powder diffractometer (Stoe STADIP) using copper $K_{\alpha 1}$ radiation (1.5406 Å) and a curved germanium monochromator. Eight equivalent data sets were collected, each from 4 to 90° in 2θ with steps of 0.1° and a counting time of 30s per step using a linear position sensitive detector (PSD). The latter is capable of measuring ca. 5° in 2θ for each step. No decomposition was observed during the measurement. A total of 726 peaks were extracted from the profile using the program EXPO.²¹ The positions of all carbon and nitrogen

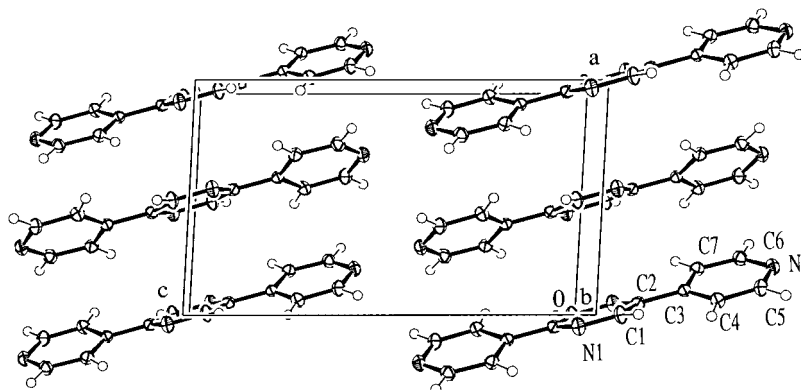


Fig. 2. ORTEP-3²⁰ crystal packing diagram of the ligand 2,5-bis(4-pyridyl)pyrazine (*4-bppz*) showing the numbering scheme.

atoms could be identified. The ligand molecule was found to possess C_i symmetry. The obtained structural model was refined in GSAS²² using the profile over the range $4^\circ < 2\theta < 90^\circ$. After the initial refinement of the scale, background and unit cell constants, the atomic positions were refined using soft constraints consisting of C—C, C—N and C—H bond distances and bond angles.²³ Hydrogen atoms were included in calculated positions to give better final agreement factors. Final refinement was carried out with low weighted soft constraints. The constraints could not be removed completely without reducing the stability of the refinement. All thermal parameters were hold fix ($U_{eq} = 25$). In the final cycles of refinement the shifts in all parameters were less than their estimated standard deviations. Neutral scattering factors were used for all atoms. No corrections were made for absorption or preferred orientation effects. The final Rietveld plot is given in Fig. 1 and fractional coordinates of the non-hydrogen atoms are listed in Table 2.

Results and discussion

Spectral characterization

The infrared spectra for the compounds *4-bppz*, *3-bppz* and **1–4** contain the characteristic

C—N and C—C vibrational frequencies for the hetero-aromatic rings of the ligand *bppz*. Evidence for the coordination of *4-bppz* and *3-bppz* was provided by the shift of ca. 20 cm^{-1} of the C=N absorption bands of the pyridine system to higher frequencies while the positions of the bands due to the C=N vibration

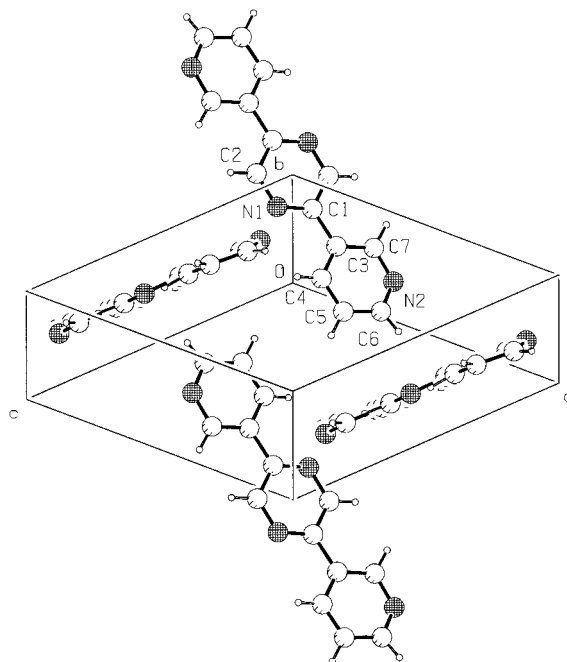


Fig. 3. PLATON¹⁹ crystal packing diagram of 2,5-bis(3-pyridyl)pyrazine (*3-bppz*) showing the numbering scheme.

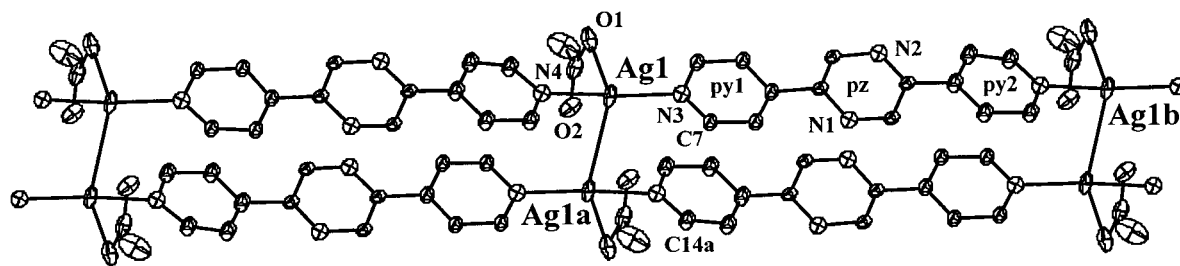


Fig. 4. PLATON¹⁹ drawing of the 1D polymer [Ag(OAc)(4-bppz)]_n (**1**), showing the numbering scheme.

of the pyrazine aromatic ring were unchanged. This can best be observed for compound **4** where there is no overlap of the C=N, C=C absorption frequencies with those from the anion. Two strong absorption bands were found for the acetate anions in complexes **1** (1570, 1409 cm⁻¹), **2** (1570, 1424 cm⁻¹), and **3** (1565, 1424 cm⁻¹).

The ¹H NMR spectrum of 4-bppz shows three signals for the symmetrical ligand. One singlet with the highest chemical shift at 9.44 ppm was observed for the hydrogen atom on the pyrazine ring, and two quadruplets (8.76 and 8.25 ppm) were observed for the hydrogen atoms connected to the pyridine rings. For 3-bppz, five signals were found in the ¹H NMR spectrum. One singlet was found for the hydrogen atom on the pyrazine ring (9.18 ppm) and four multiplets (doublets or quadruplets depending on the coupling with neighbouring hydrogen atoms) for the four hydrogen atoms in the pyridine rings. The use of mass spectroscopy reveals the molecular weight of the two ligands. No ¹H NMR or mass spectra were recorded for the coordination compounds as they are highly insoluble in all common solvents.

Structure of 4-bppz

The molecule is characterized by a center of symmetry C_i in the aromatic ring of the pyrazine. The symmetrically attached pyridine rings are twisted by about 17.7° with respect to the pyrazine ring. This relatively large angle can be explained by the minimization of interaction between the relevant hydrogen atoms of the neighboring aro-

matic rings. The arrangement of molecules in the crystal, and the numbering scheme for 4-bppz, is shown in Fig. 2.

Structure of 3-bppz

The molecular structure of this ligand was derived from X-ray powder diffraction data. The molecule is symmetrical and possesses C_i symmetry. It is almost flat with the angle between the best planes of pyrazine and the attached pyridine rings being only 2.6°. The arrangement of molecules in the unit cell is depicted in Fig. 3.

Structure of [Ag(OAc)(4-bppz)]_n (**1**)

The reaction between silver(I) acetate and 4-bppz results in the formation of a one-dimensional coordination polymer (Fig. 4). Silver(I) ions are bridged by ligand molecules, the latter using its pyridine nitrogen atoms for coordination [Ag1–N3 = 2.17(1), Ag1–N4 = 2.27(1) Å]. The distorted tetrahedral coordination sphere of the metal is completed by the acetate anion [Ag1–O1 = 2.60(1) Å] and a Ag...Ag interaction [Ag1...Ag1a = 3.077(3) Å, *a*: 1 – *x*, –*y*, 1 – *z*]. Interplanar distances of 3.55 Å (py1[^]py2a) between neighbored rings of the parallel chains were found suggesting weak π–π interactions, the shortest C...C intermolecular distance is 3.32 Å (C7...C14a). The metal-metal interaction, which is comparable to the shortest Ag...Ag contact given in the literature [Ag...Ag = 2.970(2) Å],²⁴ combined with the π–π interactions lead to the formation of linear,

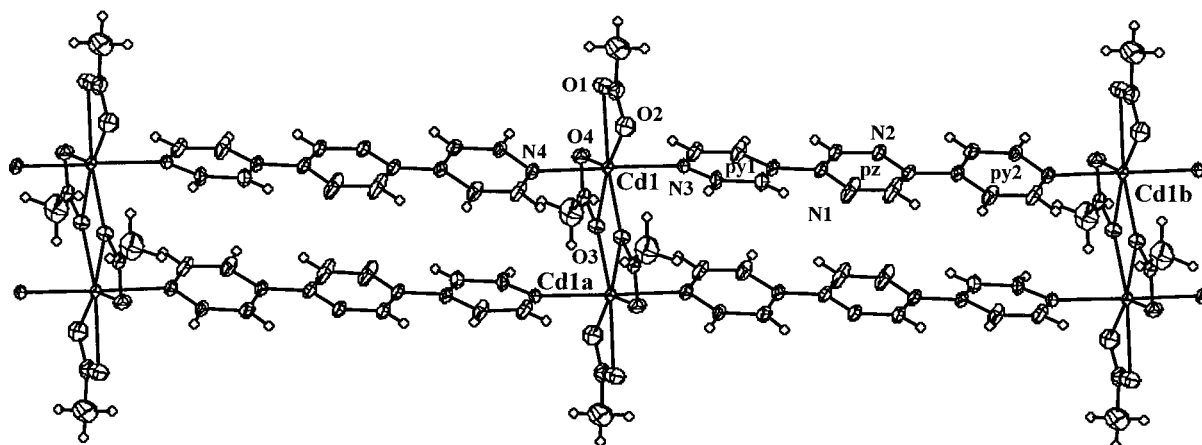


Fig. 5. The structure of the 1D polymer $[\text{Cd}(\text{OAc})_2(4\text{-bppz})]_n$ (**2**), showing the numbering scheme.

parallel double chains (Fig. 4) containing the ligand *4-bppz* in a nearly planar conformation with dihedral angles of $2.5(8)^\circ$ ($\text{py1}^\wedge\text{pz}$) and $10.9(8)^\circ$ ($\text{py2}^\wedge\text{pz}$) between the pyrazine and the two pyridine rings. Within the parallel chains, the intramolecular $\text{Ag1} \cdots \text{Ag1b}$ distance is $15.559(1) \text{ \AA}$ ($b: x - 1, y + 1, z$). Important bond distances and angles are listed in Table 3.

Structure of $[\text{Cd}(\text{OAc})_2(4\text{-bppz})(\text{MeOH})]_n$ (**2**)

The structure of this cadmium(II) complex is similar to that of the silver(I) compound **1**. The metal ions are linked by *4-bppz* molecules resulting in the formation of a one-dimensional linear

coordination polymer (Fig. 5). Two chains are connected involving two acetate anions, and the two cadmium(II) ions ($\text{Cd1} \cdots \text{Cd1a}$, $a: -x + 1, -y + 2, -z + 1$), from neighboring chains, are separated by $3.8204(5) \text{ \AA}$. The coordination sphere of the cadmium atom is completed by the coordination of a second acetate ion, so realizing a coordination number of seven. All of the cadmium–nitrogen and cadmium–oxygen distances are similar, $\text{Cd1}-\text{N}_{\text{range}} = 2.31\text{--}2.32$ and $\text{Cd1}-\text{O}_{\text{range}} = 2.33\text{--}2.45 \text{ \AA}$ (Table 2). The nearly flat *4-bppz* molecule presents dihedral angles between the best planes of pyrazine and pyridine rings of $5.6(2)^\circ$ ($\text{py1}^\wedge\text{pz}$) and $4.9(2)^\circ$ ($\text{py2}^\wedge\text{pz}$). Within the chains, the ligand separates the metal

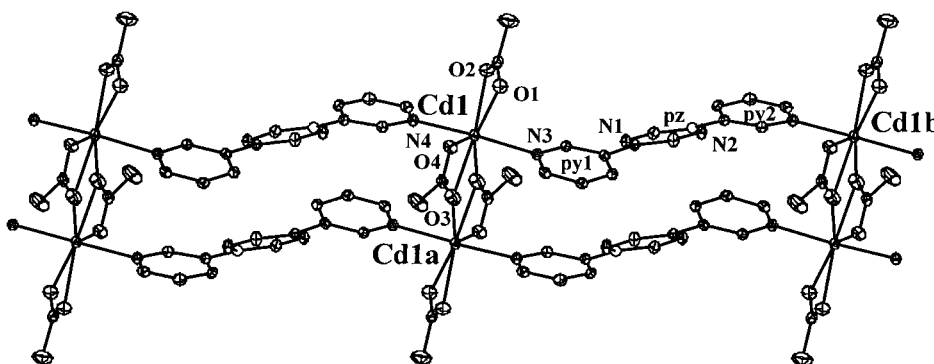


Fig. 6. The structure of the 1D polymer $[\text{Cd}(\text{OAc})_2(3\text{-bppz})]_n$ (**3**), showing the numbering scheme.

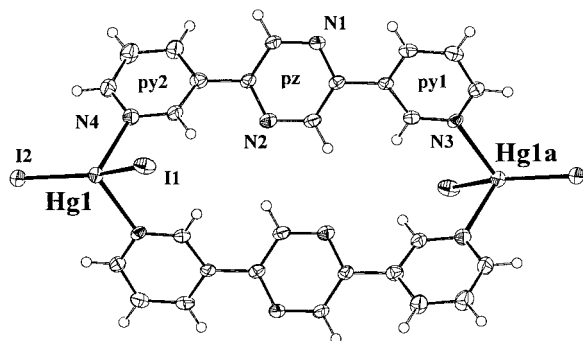


Fig. 7. The structure of the dimer $[\text{Hg}_2\text{I}_4(3\text{-bppz})_2]$ (**4**), showing the numbering scheme.

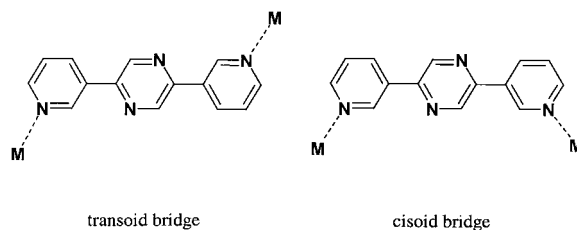
cations by $15.881(2)\text{Å}$ ($\text{Cd1} \cdots \text{Cd1b}$, b: $x + 1$, $y + 1$, $z - 1$).

Structure of $[\text{Cd}(\text{OAc})_2(3\text{-bppz})(\text{MeOH})]_n$ (**3**)

The use of the ligand *3-bppz* in the reaction with cadmium(II) acetate results in the formation of double *zigzag* chains (Fig. 6). In the homogenous chains, the cadmium(II) ions are directly connected by ligand molecules, the later using exclusively its pyridine nitrogen atoms for coordination. The coordination number of seven of the cadmium(II) ion is realized by the additional coordination of two acetate anions, both involving the two oxygen atoms in coordination and one oxygen atom coming from an acetate anion of the neighboring chain which shares its oxygen atom between two metal centers. The two cadmium(II) ions, bridged by this oxygen atom have an interchain distance of $3.8763(5)\text{Å}$ ($\text{Cd1} \cdots \text{Cd1a}$, a: $-x$, $-y + 1$, $-z + 2$) while the intrachain distance $\text{Cd1}-3\text{-bppz}-\text{Cd1b}$ (b: x , $y + 1$, $z - 1$) is $13.590(1)\text{Å}$.

Structure of $[\text{HgI}_2(3\text{-bppz})]_2$ (**4**)

The reaction of HgI_2 with *3-bppz* gave an interesting binuclear complex (Fig. 7). Two mercury atoms are interconnected by two ligand molecules forming a small cyclic organometallic compound. The ligand uses again its two pyridine nitrogen atoms for coordination with $\text{Hg}-\text{N}_{\text{py}}$ average distances of 2.46Å . For realizing the coordina-



Scheme 2. Possible bridge architectures with 2,5-bis(3-pyridyl)pyrazine.

tion to two metals, the pyridine rings are turned out of plane with respect to the pyrazine system having dihedral angles between their best planes of $28.2(2)^\circ$ ($\text{pz}^\wedge\text{py1}$) and $39.4(2)^\circ$ ($\text{pz}^\wedge\text{py2}$). The tetrahedral coordination sphere of the mercury is completed by two iodide ions having identical $\text{Hg}-\text{I}$ distances of $2.647(1)\text{Å}$.

The formation of chain or double chain compounds containing silver(I) or cadmium(II) and linear bridging ligands appears to be relatively common regarding the literature. Complexes **2** and **3** were crystallized in methanolic solutions and contain crystallized methanol molecules in their crystal structures. In the crystal, these solvent molecules are involved in hydrogen bonds with the coordinated acetate anions [$(\text{O}_{\text{methanol}}-\text{H} \cdots \text{O}_{\text{acetate}})_{\text{av}} = 2.76\text{Å}$], and have no influence on the dimensionality of the polymer.

The ligand *3-bppz* is of special interest owing to its potential to generate cisoid and transoid isomers (Scheme 2).¹¹ Schröder and coworkers found single chain and ladder type arrangements of molecules containing Cd(II) and Zn(II) with 3,6-bis(3-pyridyl)-1,2,4,5-tetrazine but with the ligand molecule always in the transoid form. In contrast, the *3-bppz* ligand realizes not only the transoid coordination form as seen in the *zigzag* double chain polymer **3**, but also the cisoid arrangement as found in the binuclear cyclic mercury(II) compound **4**.

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